THEORETICAL CHEMISTRY INSTITUTE

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WIS-TCI-388

May 25, 1970

MADISON, WISCONSIN

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ABSTRACT

The resonance theory of termolecular recombination kinetics is applied to the reaction $D + D + D_2 \longrightarrow 2D_2$. The isotope effect, i.e., the rate of deuterium recombination compared to that of hydrogen, is computed over the range 50 - 300°K. From 100° to room temperature the ratio for D/H is 0.7_1 (± 0.02), in agreement with the experimental value of Amdur (1935) and a very recent determination by Kaufman, Ham and Trainar.

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* This work received partial financial support from National Science Foundation Grant GP-7409 and NASA Grant NGL 50-002-001. Acknowledgment is also made to the Petroleum Research Fund administered by the American Chemical Society for partial support of this research.

An orbiting resonance theory for three-body recombination kinetics has been presented [1] and applied to the recombination of hydrogen atoms. Although agreement was obtained with the available experimental evidence at room temperature, the discrepancies among the various experimental values did not permit a critical check of the theory. However, a recent investigation by Kaufman et al. [2] on the relative rates of recombination for deuterium and hydrogen suggests that an accurate experimental determination of the ratio will soon be available, which could be compared with theory. Such a comparison would be advantageous since systematic errors involved in the computation of the deuterium and the hydrogen rates should be approximately the same.

In this communication we present results of the resonance theory calculation for the recombination of deuterium atoms, compatible with the earlier hydrogen work. Since the resonance theory of termolecular recombination has been fully described [1], only the results pertinent to the present case will be given.

The assumptions in the theory have been discussed in detail in connection with the $H + H$ recombination. It turns out that the quantitative criteria used to assess these assumptions do not change appreciably for the $D + D$ case.

Detailed calculations have been carried out [3], using the $^1\Sigma_g^+$ hydrogenic potential of Kolos and Wolniewicz [4], characterizing the complete bound and quasibound state spectrum of D_2. With this information it is possible to compute the resonance contribution to the deuterium recombination reaction with the same accuracy as for the hydrogen case.

Data for the relevant orbiting resonances D_2^i, labeled by their rotational and vibrational quantum numbers j and v, are given in Table 1. The relevant states represent those complexes with widths Γ_i sufficiently large ($\sim 10^{-4}$ cm^{-1}) to meet the "second criterion" of Ref. [1].

Values for the equilibrium constants K_{eq}^i are obtained directly from simple statistical mechanical considerations [1], given the energy of the complex relative to the separated atoms E_i and the rotational quantum number. The rotational de-excitation cross sections σ_i have again been computed by the renormalized modified wave number approximation [1, 5], using also the previously tested "monoenergetic approximation" [1]. As before, the choice of the three-body interaction together with the calculation of the rotational cross sections using perturbation theory represent the weakest part of the theory. The so-called vibrational relaxation mechanism, applied successfully to the hydrogen recombination reaction at elevated temperatures ($\sim 2{,}000^{\circ}K$) [6], should not be important below room temperature where rotational relaxation should play the predominant role [1].

Fig. 1 shows the results of the calculations of k_r^{D2} $(D + D + D_2)$ compared with k_r^{H2}, both systems with consistent approximations. The monoenergetic approximation would not affect the higher temperature values, but displaces the maximum in the rate to slightly lower temperatures. The ratios k_r^{D2}/k_r^{H2} should be unaltered above $100^{\circ}K$. Table 2 summarizes the relative rates and compares the resonance theory with experiment.

In calculating the deuterium rate constant, successively more resonance states were added in order to ascertain the convergence properties of $k_r^{D_2}$. The results (Table 3), show that after the addition of the 14th state, $k_r^{D_2}$ (300°K) has converged. At lower temperatures fewer states need be included. For H_2, the addition of four more quasibound states beyond the six of Ref. [1] yields an increase in $k_r^{H_2}$ of less than 2% for $T \leq 300^{\circ}K$.

The potential range parameter α and the size parameter r_{TP}^{300} defined in [1] were chosen to be identical for the two isotopic systems. The angular anisotropy parameters, a and b, of Ref. [1], different for each complex, were obtained from the rms average internuclear separations $\langle R^2 \rangle^{1/2}$.

It is interesting to note that although the resonance theory involves a detailed calculation over a relatively small (nonstatistical) set of complexes, the calculation gives the same result for the isotopic ratio of rates as a simple statistical estimate, namely $1/\sqrt{2}$. At least for this system it appears that the isotope effect is predominately determined by the relative speed factor, i.e., that above 100°K the sum, $\sum_i K_{eq}^i \sigma_i$, is (essentially) isotopically invariant. A general theoretical proof of this conjecture is not immediately apparent.

Acknowledgment

The authors gratefully acknowledge the kind cooperation of R. J. LeRoy, who performed the calculations characterizing the quasi-bound and bound state spectrum of deuterium.

TABLE 1. Characteristics of the most important resonance states for deuterium recombination.

State						Anisotropy parameters [1]	
i	j	v	$E_i(cm^{-1})$	$\langle R^2 \rangle^{1/2}$ (a.u.)	$\Gamma_i(cm^{-1})$	a	b
1	6	20	10.1	6.27	0.102	3.46	2.54
2	7	20	37.4	6.73	16.9	3.51	2.63
3	10	19	57.4	5.62	0.474	3.35	2.34
4	11	19	115.	6.12	24.8	3.44	2.50
5	13	18	100.	5.12	0.054	3.21	2.07
6	14	18	198.	5.63	15.8	3.35	2.34
7	16	17	204.	4.90	0.236	3.13	1.95
8	17	17	331.	5.36	23.9	3.30	2.22
9	18	16	185.	4.48	$1.6X10^{-4}$	2.96	1.71
10	19	16	382.	4.85	2.86	3.12	1.93
11	21	15	425.	4.47	0.128	2.95	1.75
12	22	15	626.	4.93	21.1	3.14	1.97
13	23	14	478.	4.21	0.006	2.82	1.55
14	24	14	742.	4.59	7.10	3.00	1.78

TABLE 2. Relative recombination constants for deuterium and hydrogen.

Reference	$k_r^{D_2}/k_r^{H_2}$	T(°K)
Amdur[a]	0.74 ± 0.04	303
Kaufman et al.[b]	0.7	298
Present calculations via resonance theory[c]	0.71 ± 0.02	100 to 300

(a) Ref. [7].

(b) Ref. [2].

(c) Potential parameters [1] are $\alpha = 2.0$ a.u.$^{-1}$ and $r_{TP}^{300} = 4.5$ a.u.

TABLE 3. Convergence of the calculated termolecular recombination constant for deuterium at 300°K[a].

i states included	$10^{-15}\ k_r^{D_2}$ ($cm^6 mole^{-2} sec^{-1}$)
1 to 10	3.31
1 to 11	3.33
1 to 12	3.35
1 to 13	3.36
1 to 14	3.36

(a) Potential parameters [1] are $\alpha = 2.0$ a.u.$^{-1}$ and $r_{TP}^{300} = 4.5$ a.u., same as for H_2.

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Figure Caption

Fig. 1. Calculated recombination rate constants for H_2 and D_2.

Figure 1